

PB-237 900-T

EFFICIENCY OF OIL-SPILL REMOVERS

Pierre Michel

Environmental Protection Agency
Research Triangle Park, North Carolina

1974

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U. S. DEPARTMENT OF COMMERCE

312019

PB 237 900 -T

NTIS

EPA-TR 43-75

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[Efficacite des produits antipetrole]

Rev. Trav. Inst. Peches marit., 36 (1), 1972, p. 85-102

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U S Department of Commerce
Springfield VA 22151

Translated for the
ENVIRONMENTAL PROTECTION AGENCY
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Introduction

In recent years, as petroleum pollution has increased, we have seen commercial products appear on the market to combat that pollution. These products, metal degreasers, ingredients for plastics, absorbents for use in cleaning up industrial effluents, and the like, are not new. Only their application is very different. There are other products that have been developed especially to attempt to solve this new problem. The number and variety of these products is such that choice is not easy because the consequences can be good, or catastrophic, depending on whether the products are, or are not, harmful to the environment one wants to protect.

The Institut des Pêches [Fisheries Institute] has received a total of 101 products for purposes of comparative study and selection of the best of them. It was impossible to test all of these products in situ. But some were tested on the occasions of the different incidents that have occurred in recent years. And it was during these tests that there arose an awareness that it is extremely difficult to determine just how much oil there is that must be eliminated, how efficient the clean-up is, and, in essence, how efficient a particular product may be. Equally impossible is the obtaining of reproducible conditions in a natural environment. Any attempt to compare two products is hazardous, and there is no solution to the problem when one is dealing with about one hundred.

We therefore did our study under laboratory conditions, using standard methods in order to obtain accurate, reproducible, and exploitable results.

There is no question of the fact that we had to hedge on natural conditions somewhat, but not too much, and since the study was to be comparative in nature, we could refer to products already tested in situ to put the study as a whole into its real context. When it came to the selection of the tests that would be made we had to take into consideration the different categories of oil-spill removers and to select the reference hydrocarbons.

Different types of oil-spill removers

Three categories were established, according to how they react with hydrocarbons.

1. The emulsifiers are liquids, the base of which is organic solvents, and surface-active products, the purpose of which is the immediate elimination of the oil on the surface, or by getting rid of the oil by converting it into a fine emulsion. After that the degradation of the oil by marine bacteria is much more rapid and its dispersion better.

2. The agglomerants are low density powders that absorb the surface hydrocarbons and facilitate their recovery.

3. The precipitants also are absorbent powders, but are heavier than water, and thus cause the oil to settle on the sea bottom.

We, in the course of this study, shall assign each of these products a reference number preceded by the letters E, A, or P, depending on whether the product is an emulsifier, an agglomerant, or a precipitant. Test methods will differ, depending on the nature of the product tested. We shall make a separate study of the emulsifiers that fall into a special category, as well as of pulverizers, a term that encompasses the agglomerants and the precipitants that are similar in nature, and differ only in the final elimination phase.

Choice of reference oils

There was every reason to think that the efficiency of a product would vary with the nature of the oil that had to be eliminated, and particularly with its viscosity. So it was important that reference could be made to oils from different sources. Moreover, the greatest part of the 500 million tons of oil moving off the French coasts comes from the Middle East. We therefore selected a crude oil from Kuwait, and another from Syria. And aware of the fact that Algeria furnishes 50% of our national consumption, something in the neighborhood of 50 million tons, we selected as our principal reference a crude from Edjelé. The characteristics of these three oils are:

	Edjelé	Kuwait	Syria
Density 15/4	0.847	0.869	0.939
Viscosity, CSK	12.5/20°C	18/20°C	107/40°C
Pour point (°C)	- 6	- 32	- 27
% paraffin	3.7	5.9	1.0

It should be pointed out that these oils cover quite a wide range since two of the light crudes are quite fluid, and the heavy one is much more viscous.

I. Emulsifiers.

1. Bibliographic review of efficiency tests.

The elimination of oil spills at sea is not a new problem, and a great many studies already have been made around the world to test products developed to emulsify the oil. The complexity of the methods used varies, and the results to be anticipated from the use of the different products vary greatly as well.

The U. S. Navy has been concerned with eliminating pollution attributed to its own ships since 1961. This is why it is a military specification

that sets the properties required of emulsifiers, and the manner in which they are to be measured. This specification also sets the colorimetric emulsifying ability of a product under test by forming an emulsion consisting of the product and a chloroform extract of the oil in question. The stability of this emulsion is evaluated by eye only 6 hours after its formation.

So far as cleaning up the coasts is concerned, J. C. Taylor (1962) proposes taking a column of sand from which an attempt is made to eliminate the oil by percolation as a point of reference. He then develops a gravimetric measurement of the oil eliminated on the one hand, and of the fraction remaining fixed in the sand on the other, after carbon tetrachloride extraction. This same author advocates extraction of the oil that still remains after one hour in order to determine the stability of the emulsions.

These methods have not been improved by subsequent efforts. Variants are primarily the result of concern for simplification. G. Kondo et al (1969) advance, among others, the concepts of dispersibility and diffusibility, and while certainly interesting, are not definitive. Moreover, an increase in selection criteria is not desirable because the most important criteria can be hidden in the totality of the approach. Other authors use very quick tests. Thus, J. E. Smith (1968) is content to make a visual observation of emulsions formed, and to record their evolution in accordance with the volume of the surface layer. But the volume of this floating phase sometimes is greater than the quantity of hydrocarbon and the surface-active set in motion (the case of water-oil emulsions). The test thus has the advantage of being easy to use, and is practical for differentiating between a limited number of products over an extended period of time. J. C. Neirinckx (1970) tested 23 emulsifiers in this way. His idea, among other things, was to

study the correlations between efficiency and product solubility on the one hand, and between efficiency and surface tension on the other. The conclusions are not clear cut, however, because of the imprecision of the method used. Finally, L. R. Beynon (1970) used this same test and compared the results with those obtained under the same conditions with a standard containing 30% Manoxol O.T. in a petroleum ether solution. However, the results were checked visually, and thus were subjective.

2. Choice of methods used.

Three parameters are indispensable in the final selection of emulsifiers; emulsifying power, cleaning power, and emulsion stability. Measurement of the emulsifying power will provide a good indication of ability to disperse oil films off coasts. Cleaning power will be more useful in the case of oil that has reached the coast. In these two cases, good stability of the emulsions is indispensable in order to avoid having the oil break up into isolated films that are difficult to eliminate, and which always wind up on the coasts.

Furthermore, emulsification of the oil is but one stage in its elimination. The spectacular side of the pollution is made to disappear, but the hydrocarbons remain in the marine environment for long periods of time. All oils can, in principle, be degraded by the action of bacteria. Zobell (1962), on the basis of the rapidity with which marine bacteria oxidize different oils under laboratory conditions, estimates that the elimination rate in the sea could reach from 100 to 960 mg/m³/day. This rate is influenced by the abundance of microorganisms present and their type, the quantity of dissolved oxygen, the temperature, and the dispersion of the oil in the water. It is a practical impossibility to vary the first

factors artificially. We shall have to watch out for the time, on the other hand, when the oil will be reduced to very tiny droplets by a dispersant that will not be harmful to the bacterial flora.

The tests we adopted to determine emulsifying power and emulsion stability were adapted from those used by the U. S. Navy and J. C. Taylor. We defined certain of the experimental factors to permit us to also evaluate the size of the dispersed droplets. As a matter of fact, these tests are based on the kinetics of the reassembly of hydrocarbons, so Stock's formula

$$V = \frac{2 \epsilon R^2 (d_1 - d_2)}{9 \eta}$$

can be used. Here V is the rate at which the droplets reassemble, η is the viscosity of the sea water, d_1 is the density of the sea water, and d_2 is the density of the reference oil. The radius, R, of the droplets can be deduced. Using Edjelé crude oil, and the method of operation described in what follows, we were able to compare the emulsifying power as a percentage of the oil reduced to droplets less than 50 μ , approximately, in radius. Stability of the emulsions then corresponds to the percentage of oil reduced to droplets less than 15 μ in radius in terms of the oil emulsified.

We adapted J. C. Taylor's method to measure cleaning power so we could use it for the more viscous oils, such as certain of the crudes, after their light fractions have evaporated in the course of prolonged stay in the sea. Moreover, we came around to the selection of a different method of operation where the Edjelé and Kuwait oils were concerned on the one hand, and the Syrian oil was concerned on the other, for in the case of the latter the use of a rigid test would bring the results down to the lowest level, and would permit no selection to be made later on.

We thought it would be useful to add to these three measures, which by the way are indispensable if the proposed goal of the study is to be met, the measurement of certain physicochemical parameters of the products in order to verify the eventual existence of correlations between these parameters and the efficiency of the products on the one hand, and their toxicity on the other. To this end, we measured their density, viscosity, solubility in sea water, pH in a 10% solution, anionic detergent content, surface tension in a 10% solution and 100 ppm, and, finally, the rate at which they are eliminated from the natural environment.

3. Methodology.

(a) Measurement of emulsifying power.

The equipment shown in Figure 1 is essentially a container with a capacity of about fifteen liters, with a petcock for drawing off samples installed about one-third of the height. An agitator

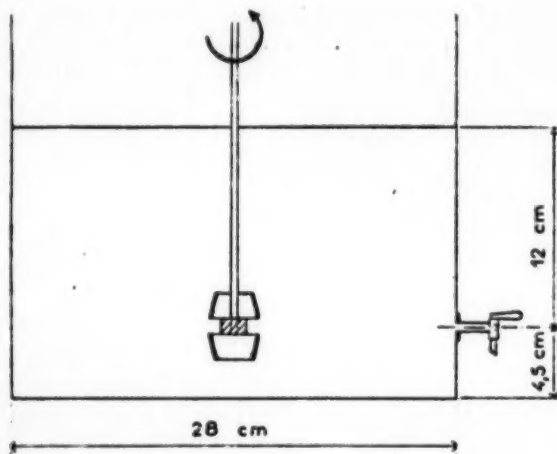


Figure 1. Equipment for emulsifying the oil.

on a vertical shaft is used to mix the emulsion. A thorough mixture of 5 ml of Saharan oil and 5 ml of the product to be tested was prepared first, and then was added to 10 liters of sea water in the container.

The mixture then was agitated for 10 minutes at 1000 rpm, after which two 500 ml samples were drawn from the container. One sample, A, was drawn one minute after agitation ceased and was used to determine emulsifying power. Sample B, the other sample withdrawn, was taken after 10 minutes at rest and was used to determine emulsion stability.

The oil was extracted from sample A three times with 15 ml of chloroform. The three fractions together were made up to 50 ml and dried by anhydrous sodium sulfate. This was followed by colorimetric determination at 480 nm, with the reference a standard scale of the same oil. If c is the concentration of oil in the extract, and if the emulsifying power is the percentage of oil emulsified by 1 ml of the test product, then

$$EP \% = 2 \times 10^4 c .$$

(b) Measurement of emulsion stability.

Sample B was treated and subjected to colorimetric analysis in the same manner as was sample A. Let c' be the concentration of oil in the extract. The emulsion stability can then be expressed in terms of the oil effectively emulsified at the outset

$$ES \% = 100(c'/c) .$$

(c) Measurement of cleaning power.

Use was made of a 12 mm diameter fritted glass column filled to a height of 20 cm with Fontainebleau sand, the grains of which measured between 250 and 400 μ . This column was mounted on a filtering flask to speed up the passage of successive liquids. 100 ml of sea water were poured into the column and when the water level was flush with the sand 1 ml of the oil was placed on the surface without staining the walls. There was little variation in the height at which the oil was fixed, and

this made it possible to check on how well the column performed the preliminary cleaning. Then, without reduced pressure, the following were passed in succession:

- | | |
|-----------------------------|--------------------------|
| (a) 1 ml of the emulsifier; | (d) 45 ml of chloroform; |
| (b) 100 ml of sea water; | (e) 5 ml of acetone; |
| (c) 2 ml of acetone; | (f) 100 ml of sea water. |

Operations (a) and (b) took out some of the oil. The residue was carried over by the (c) and (d) fractions, which then were added to each other, brought up to 50 ml, and dried by anhydrous sodium sulfate. The dissolved oil was subjected to colorimetry at 480 nm. Operations (e) and (f) are essential for restoring the column before the next test. If C is the concentration of oil in the extract, the cleaning power can be expressed in the form

$$CP \% = 100(1 - 0.05 \times C) .$$

It corresponds to the percentage of oil removed under the test conditions.

Note. In order to avoid the almost zero results with each of the products in the case of the Syrian oil we took a different approach and, all other things being equal, reduced the quantity of oil used to 0.5 ml. Moreover, the small percentage of volatile fractions permitted us, in this case, to make a gravimetric determination of the oil recovered in the column.

(d) Measurement of product elimination rate.

A 1% aqueous solution of the products was surface aerated with compressed air for two weeks without foam formation. Product elimination was measured at the outset, and after 2, 7, and 14 days, by total oxidation of organic matter in sulfur dichromate. It then was easy to deduce the percentages eliminated and to draw the corresponding curves.

(e) Physicochemical measurements.

The viscosities of the emulsifiers were measured at

20, or 40°C, by the capillary tube flow method. The pH was measured by the electrometric method, and Dognon and Abribat's method (1941) was used to measure the surface tension. In the latter case, the solutions were first left to rest for two hours so the subsequent measurements would be stable. Finally, the anionic detergent determination was made with dilute solutions according to Abott (1962).

4. Results and interpretation.

Table 1 lists all results of product efficiency measurements. However, it would be well to take these data separately to garner from them the best available information. In point of fact, it always is dangerous to take test results obtained in the laboratory and attempt to apply them to real life. Nevertheless, it is possible to draw conclusions that would not have been as clear had the tests been conducted at sea, because the various factors selected were the optimums.

(a) Emulsifying power. Emulsion stability.

The measurement of emulsifying power was made under conditions that were more favorable than those that would have been found in practise because of the proportions used, the premixing of the oil and detergent, as well as the vigorous agitation provided in making up the emulsion. The use of equal parts of detergent and oil may seem excessive, but was decided upon in order to obtain stable emulsions. Weaker mixtures of certain of the products could have been used, of course, but in view of the preliminary tests, we had to hold to this proportion in order to standardize the tests. There is no question, on the other hand, that the quantities recommended by some of the manufacturers are clearly underestimated. Furthermore, the premixing of oil and emulsifier enhances the action of the latter, slowing, as it does, the solubility of the emulsifier

Números 1	Pouvoir émulsionnant 2	Stabilité des émulsions 3	Pouvoir nettoyant moyen 4	Coefficient d'efficacité 5
E 1	98	55	65	0.72
E 2	94	60	82	0.78
E 3	80	62	82	0.74
E 4	92	90	42	0.74
E 5	100	80	80	0.86
E 6	83	68	74	0.75
E 7			53	
E 8	68	43	92	0.67
E 9	88	91	64	0.81
E 10	97	100	72	0.89
E 11	96	82	24	0.67
E 12	83	70	70	0.74
E 13	87	98	85	0.90
E 14	89	79	75	0.78
E 15	73	70	69	0.70
E 16	89	72	65	0.75
E 17	90	94	32	0.72
E 18	89	93	27	0.69
E 19	96	92	54	0.80
E 20	98	88	85	0.90
E 21	90	96	76	0.87
E 22	83	92	65	0.80
E 23	83	74	22	0.59
E 24	96	59	74	0.76
E 25	81	41	5	0.42
E 26	83	86	62	0.77
E 27	99	88	75	0.87
E 28	70	86	50	0.68
E 29	88	96	71	0.85
E 30	84	94	57	0.78
E 31	93	96	80	0.89
E 32	95	89	55	0.79
E 33	92	94	23	0.69
E 34	94	98	70	0.87
E 35	89	58	47	0.64
E 36	79	97	85	0.87
E 37	88	93	84	0.88
E 38	91	50	81	0.74
E 39	96	98	57	0.83
E 40	98	99	21	0.72
E 41	97	100	91	0.96
E 42	92	92	70	0.84
E 43	92	92	80	0.88
E 44	95	90	72	0.85
E 45	97	96		
E 46	93	100	83	0.92
E 47	95	96	73	0.88
E 48	91	51	72	0.71
E 49	99	80	42	0.73
E 50	100	53	8	0.53
E 51	77	48	56	0.60
E 52	87	95	72	0.84
E 53	87	99	76	0.87
E 54	100	88	40	0.76
E 55	92	70	77	0.79
E 56	72	95	71	0.79
E 59	80	44	71	0.65
E 60	93	40	25	0.52
E 61	91	49	33	0.57

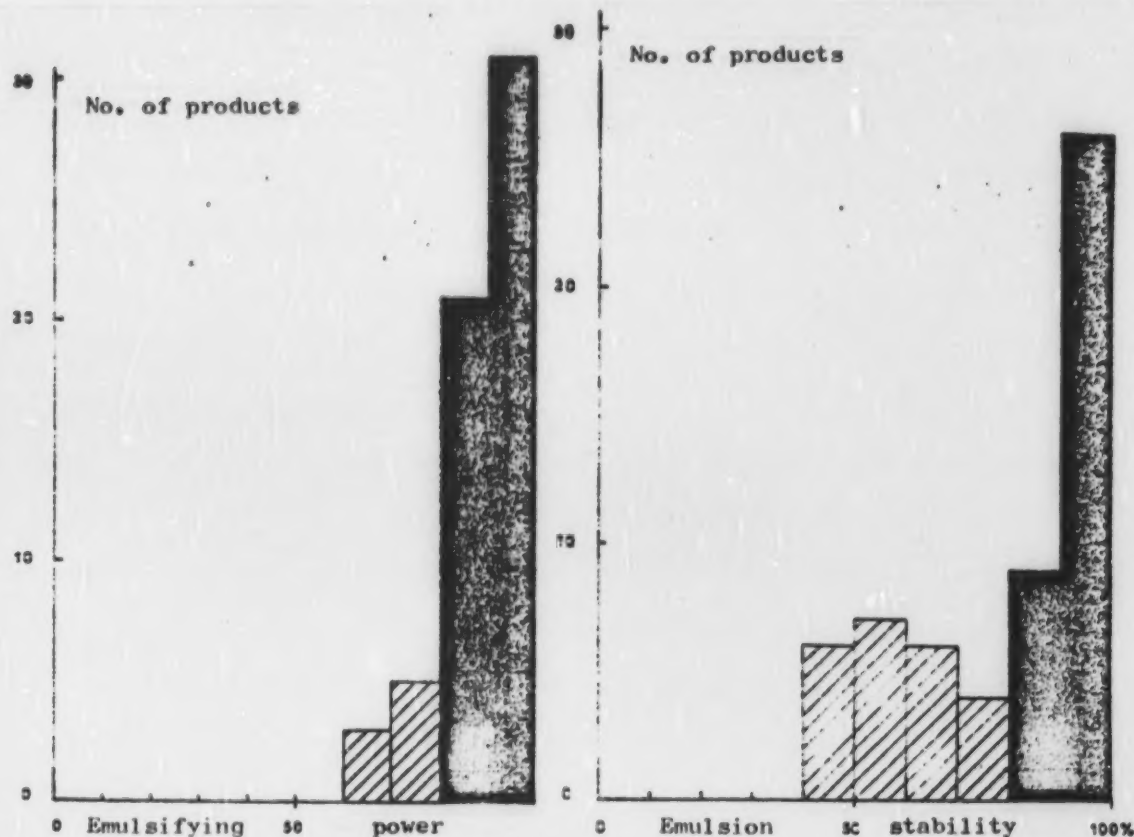
TABLE 1. Column headings: 1 - Test No.; 2 - Emulsifying power;
3 - Emulsion stability; 4 - Cleaning power, mean; 5 - Efficiency.

in the water to the detriment of the hydrocarbon. This condition is a long way from being realized in fact when we consider the tremendous disparity between the masses of water and of oil present. This action is not insignificant, even in the case of products that are only slightly soluble in water. Finally, agitation is much stronger than under natural conditions, but this latter advantage is partially balanced by the complete cessation of agitation during the period preceding the taking of the sample.

Study of the distribution of the results thus obtained (Figures 2, 3) shows that the products are good most often in the case of emulsifying power, since 86% of the products proved to grade out at better than 80. Emulsion stability frequently was poorer, with only 60% of the products showing this same value. But since the results are a function of the proportions used, one ought not take too much satisfaction from these results because a good product ought to be efficient in proportions lower than those used by a factor of 10. We often had much more encouraging results during tests at sea, but it is very difficult in such cases to verify the permanent disappearance of an oil film, and to establish the part attributable to incomplete emulsification, and that attributable to emulsion instability. Moreover, evaluation of the results is made visually, and this is quite subjective. It is essential that these tests be carried out at half-scale in order to test the most efficient way to put these products to work, as well as to monitor the validity of the laboratory results. However, these half-scale tests cannot reasonably be carried out except with the products already preselected.

(b) Cleaning power.

Cleaning rocks and sand stained by oil calls for the properties cited above, because in this case it clearly is a matter of



Figures 2 and 3. Distribution of products according to their emulsifying power (left), and emulsion stability (right).

making as stable an emulsion as possible. But such emulsification assumes that the petroleum products already have been detached from their support. This operation is difficult to bring off. Resort must be had to very special detergent properties. The cleaning operation along coasts takes place at low tide, in practise, and the emulsifier that is spread on the oil is not subjected to mechanical action of any kind prior to the practical rinsing, either by torch, or the simple action of the rising tide. So it

thus is necessary that the oil-detergent mixture develop simply as a result of the reciprocal solubility action, and not by premixing. Accordingly, the choice of a good solvent, used in adequate proportions, becomes highly important. And this too certainly must be the reason why there is such a big difference between elimination of Sahara oils and Kuwait oils, which contain a high percentage of light fractions, and the Syrian oil, which is richer in heavy fractions, and in which surface-active products migrate less rapidly.

This phenomenon is quite apparent in view of the results. Figure 4 shows the differences in the ability of the products to cope with the three reference oils. Outstanding is the fact that the thirty best products behave in virtually the same way in the case of the two light crudes. The difference therefore is exclusively in the case of the more viscous oil because, with one exception, the corresponding rating always is below that of the light oils. Given the fact that in the case of the Syrian oil we doubled the proportion of detergent normally used, the quantity of oil entrained would have had to be greater, so this weakness is characteristic.

The risk of having to deal with viscous oil is the more frequent one because the oil becomes more viscous as the light fractions evaporate during the days at sea before the oil reaches the coast. Oil residues sometimes are much more cohesive than the reference oil we consider the most difficult to handle. We are not concerned with trying to make the tar "balls" that are more or less solid disappear. These float up onto the beaches and it is more advantageous to remove them mechanically. Yet even in the case of the very viscous crudes the proportion of emulsifier used is such that it is desirable to limit the use of these products to cases of absolute necessity.

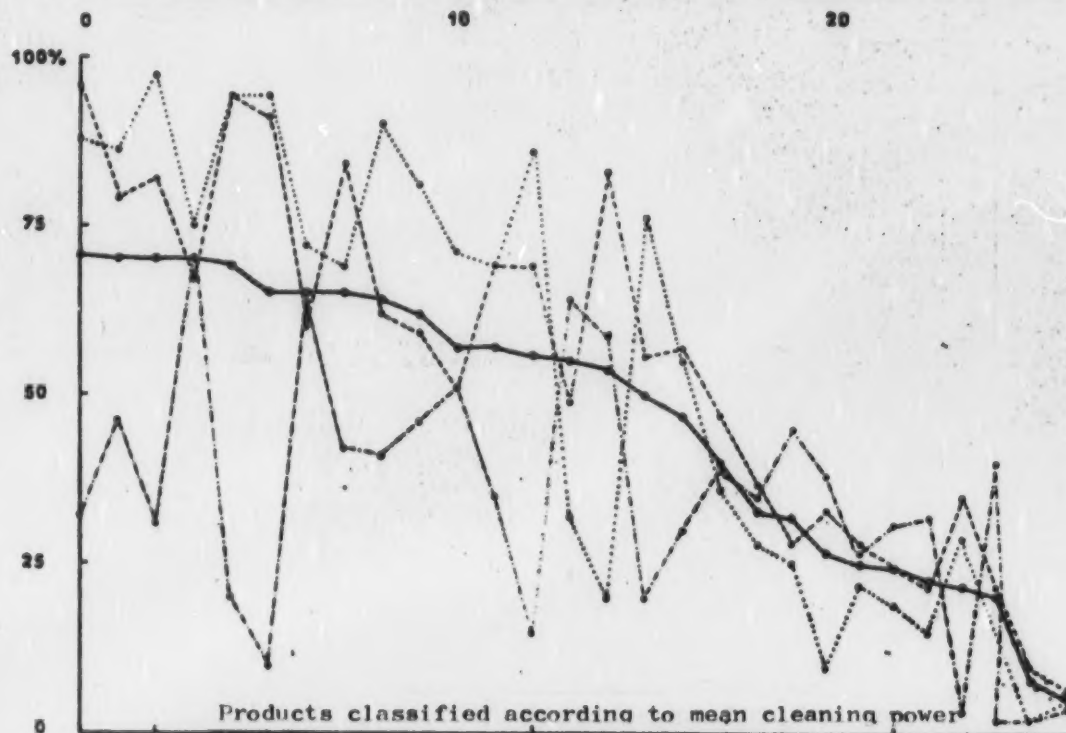
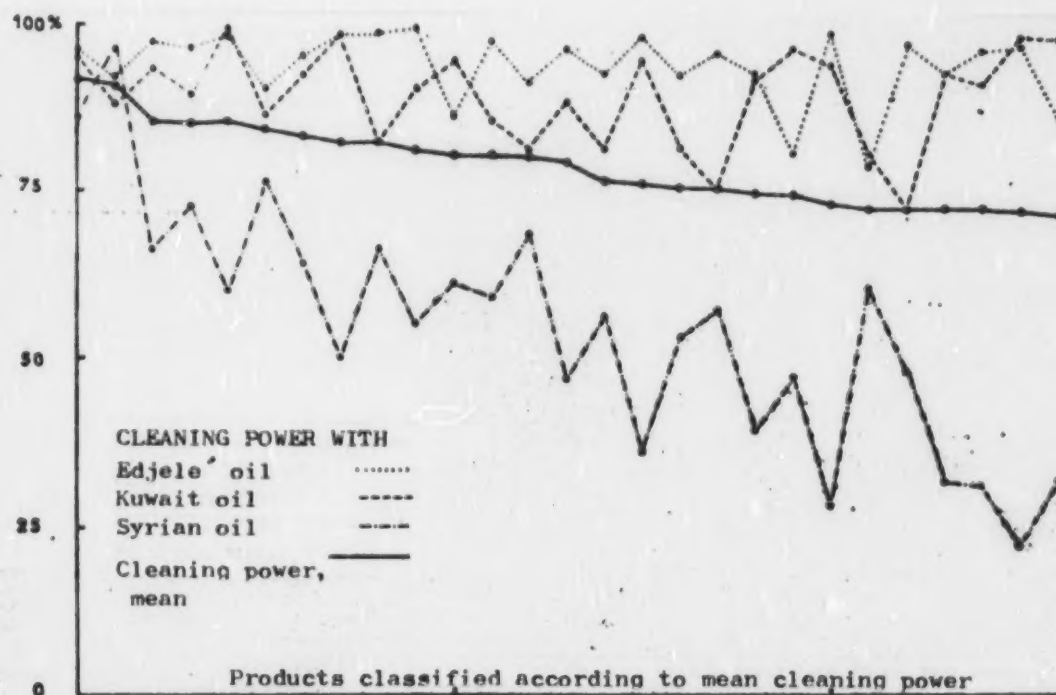
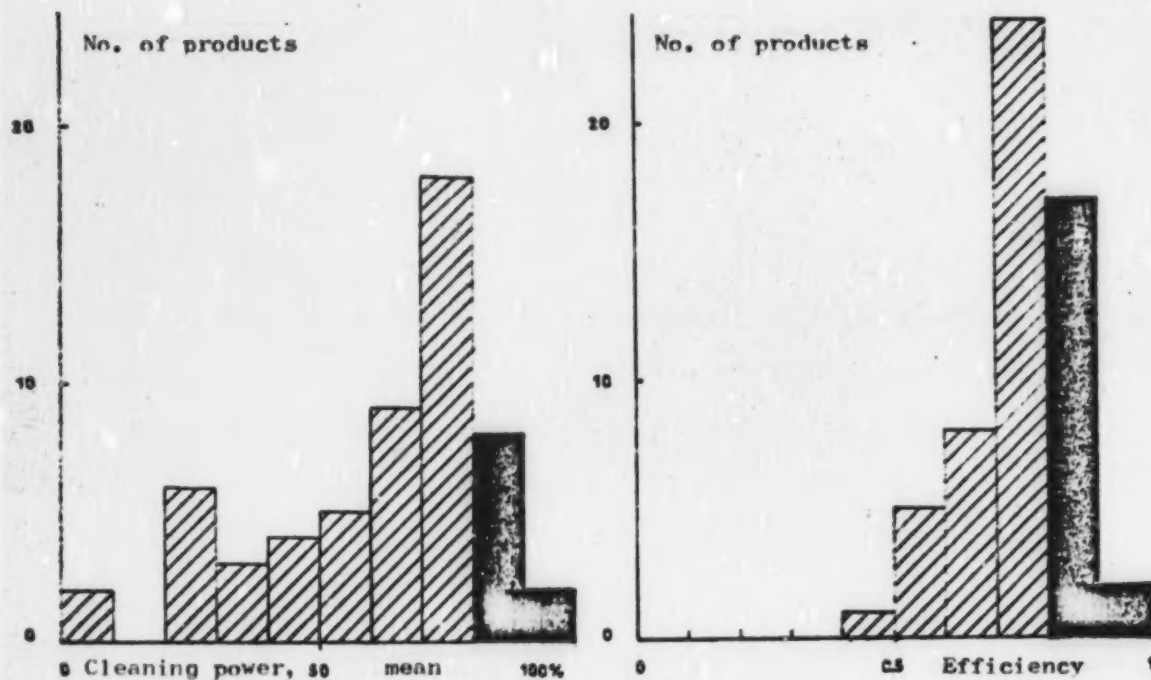


Figure 4. Cleaning power comparison for the three reference oils. Products are classified according to mean cleaning power, decreasing from 1 to 26 (top) and 27 to 55 (bottom).

1 Numéros	2 Densité 20° C	3 Viscosité CSK	4 Solubilité eau de mer	5 pH à 10%	6 Tension superficielle		7 Détergents anioniques
					10 ppm	100 ppm	
E 1	0.760	2.4	13.5	7.82	48	34	
E 2	1.011	176.8	> 200	9.16	42	29	
E 3	0.998	4.9	> 200	7.85	43	29.5	
E 4	0.795	1.9	122	7.75	43	29	
E 5	0.954	15.9	2.5	7.19	42	30.5	
E 6	0.902	3.2	114	7.80	47	35	
E 8	1.040	116.6	197	7.55	49	35	16
E 9	0.906	5.3	86	6.86	43.5	34	
E 10	0.990	212.5	> 200	2.28	38	34	2
E 11	1.003	100.0	> 200	7.73	55	42	
E 12	1.060	326.0	> 200	7.95	41.5	30	
E 13	1.025		> 200	8.15	52	38	
E 14	1.032	140.5	> 200	8.12	46	32	
E 15	1.61	301.3	> 200	7.72	42	31	
E 16	1.064	105.3	> 200	7.91	49	31	
E 17	0.808	5.0	195	7.74	57	51	7
E 18	0.826	8.7	195	7.45	59	42.5	6.5
E 19	0.550	14.0	188	7.85	55	40	7
E 20	1.124	329.3	200	7.85	42	30	16
E 21	0.930	8.1	181	7.32	52	31	13
E 22	1.042	2.0	> 200	7.54	43	29.5	
E 23	1.073	3.0	> 200	8.09	66	38.5	3
E 24	1.055	114.7	> 200	8.04	57	36	12.5
E 25	1.556		164	2.21	72	70	
E 26	0.810	2.2	137	7.58	65	40	
E 27	0.945	5.1	159	7.83	48	29	16.5
E 28	0.992	433.9	7.6	7.84	37	30	
E 29	1.027	99.4	> 200	7.68	40	30	
E 30	0.812	2.2	166	7.31	53	37	
E 31	0.533	3.4	3.5	7.69	40	29	
E 32	0.551	2.2	116	7.02	46	31.5	
E 33	0.955	45.0	> 200	7.94	53	44	
E 34	1.038	353.2	> 200	7.93	38	30	
E 35	0.790	2.4	145	6.92	69	48	
E 36	0.855	6.4	14	7.75	45	29	
E 37	0.912	3.8	151	7.96	48	36	
E 38	1.034	102.6	> 200	7.90	48	31	18
E 39	0.795	2.6	119	7.98	29	26	
E 41	0.594	9.1	199	7.64	49	40	
E 45	0.960	190.4	33	8.04	45	39	
E 47	0.520	5.3	44	7.86	48	43	
E 48	1.025	307.0	> 200	8.71	49	34	10
E 49	0.755	1.6	55	7.76	50	43	
E 50	0.956	129.3	195	7.81	49	45	4
E 52	0.540	1.6	51	7.37	48	30	
E 53	0.536	1.9	41	7.94	56	40	
E 54	0.915	4.3	195	6.02	56	36	
E 57	1.035	436.5	> 200	7.52	48	32	31
E 58	1.062	324.5	> 200	7.98	41	31	
E 59	1.049	3.2	> 200	9.16	57	45	
E 60	1.001	101.4	> 200	7.85	53	47	
E 61	0.849	14.8	1.2	7.47	29	23	

TABLE 2. Column headings: 1 - Test No.; 2 - Density; 3 - Viscosity;
4 - Solubility in sea water; 5 - pH at 10%; 6 - Surface tension;
7 - Anionic detergents.



Figures 5 and 6. Distribution of products according to their mean cleaning power (left) and efficiency (right).

Finally, regardless of the reference oil used, we found that the sand column appeared to be quite clean after 80% to 90% of the hydrocarbons had been filtered out in the column, despite the fact that a substantial proportion of pollutant still remained. This fact gives some idea as to the limits of visual evaluations in this matter, and also some idea of the subjectivity of this approach.

(c) Efficiency.

We have reviewed the three parameters we selected for use in deciding on which products were best suited for eliminating petroleum pollution; emulsifying power, cleaning power, and emulsion stability. They are the most interesting of the indications, particularly if they are

related. We therefore combined these three values so they could be applied in the form of an overall rating that we call product efficiency

$$\text{Efficiency} = (\text{EP \%} + \text{ES \%} + \text{MCP \%})/300 .$$

The emulsifying power (EP %) and emulsion stability (ES %) already have been defined. So far as the cleaning power is concerned, we have introduced the mean cleaning power (MCP %) rather than adding the values obtained for each of the three oils, so as to avoid giving this factor a greater relative importance than it should have (Figure 5).

Given this definition, the efficiency ranges from 0 to 1. In fact, if Table 1 is taken into consideration this factor varies from 0.42 to 0.98, so good differentiation between products already is available. The mean is 0.778, and is a better representation of the distribution of the results, as may be seen from Figure 6. It is difficult to assign any great importance to this factor in absolute terms, and its sole purpose, so far as we were concerned, was to provide a means for making a comparative study of the products. Moreover, the efficiency was greater than 0.8 in 33% of the cases, so this figure could be used as the selection threshold. In another connection, fixing this threshold at an elevated level implies that each of the parameters with an effect on efficiency retains its importance. In point of fact, none of the products selected had a partial rating less than 50%, and these descending ratings rarely fell below 65%. So one can be sure of retaining those products that can be used equally well on the high seas or along the coast, without risk of the hydrocarbon slicks reforming as a result of emulsion instability. The ultimate effect of the preselected products on marine flora and fauna is yet another factor that will have to be examined in the aftermath of this study.

5. Relationships between physical properties and efficiency.

Table 2 lists the physicochemical properties of the emulsifiers studied. The connections that could exist between these properties and the efficiency of the products sometimes are difficult to show, probably because of the complexity and the diversity of the formulations. The influence of one parameter would be easy to show, if it could be varied in isolation, but in the present case a score or more of parameters could vary simultaneously, and it is difficult to know what to assign to each. Study of the physical properties is the only means available for comparing products with each other, simply because product components differ from one product to another.

(a) Effect of density and viscosity.

As one might be led to suspect, in the majority of cases the products with light solvent bases (density below 0.9) are not very viscous, but they are when the proportion of solvent is less, or when the products use a heavy solvent base. This is why we thought it well to make a simultaneous study of the effect of these two parameters on efficiency. This effect would, moreover, appear to be very little, either on efficiency or on the three parameters that go to make up the efficiency. It would show up simply on the difference in capacity to clean up the different oils as a function of their viscosity. Still, there is no general rule that can be formulated. The presence of light solvents, those with low density and viscosity, most often bring about a definite improvement in the elimination of Syrian oil (viscous). The opposite action, that is, the effect obtained in eliminating light crudes (Sahara and Kuwait) with products with greater densities and viscosities, is less clear.

(b) Effect of solubility in sea water.

According to a very commonly held idea, fat-soluble detergents would be more efficient than other types of detergents in emulsifying oil, and in providing greater emulsion stability. According to our results this is not necessarily so. In fact there are some water-soluble products just as efficient, if not more so. The rare products studied that were insoluble in water in fact cover the whole of the efficiency range. This is why we are wary of setting down a law one way or the other.

(c) Effect of surface tension.

If there is one specific property possessed by emulsifiers it is their capacity to lower surface tension in the solution. Measurements made for 10 and 100 ppm in aqueous solutions and the results of the latter of these concentrations were so close to the former that a separate interpretation was impossible. The variation in the efficiency as a function of the surface tension for 10 ppm aqueous solutions (Figure 7) clearly shows that the efficiency is greater the lower the surface tension. Of course, the scatter of the points in the figure shows, if that were necessary, that this factor does not stand alone, but it surely is one of the more important ones.

Looking at the proportion of anionic detergents contained in the products, one sees no special effect of such content on efficiency. This is an important point, for if the type of detergent used only influences the slope of the surface tension curve there is more latitude in the formulation of a new product, in selecting a component that satisfactorily lowers the surface tension while at the same time providing a product with a toxicity as low as possible and one that is readily degradable.

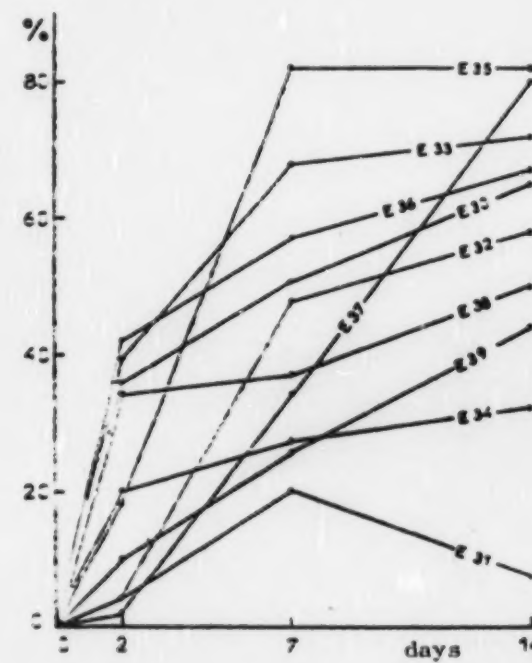
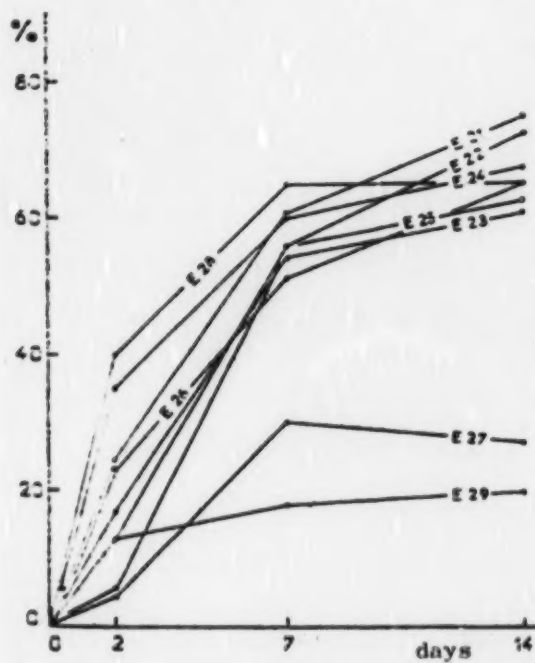
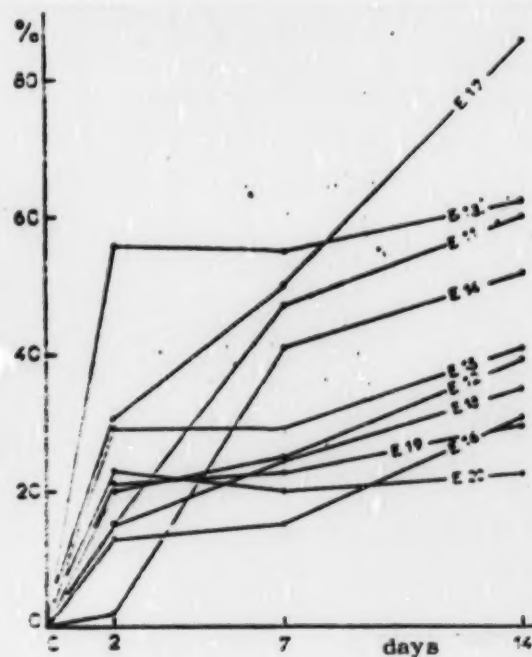
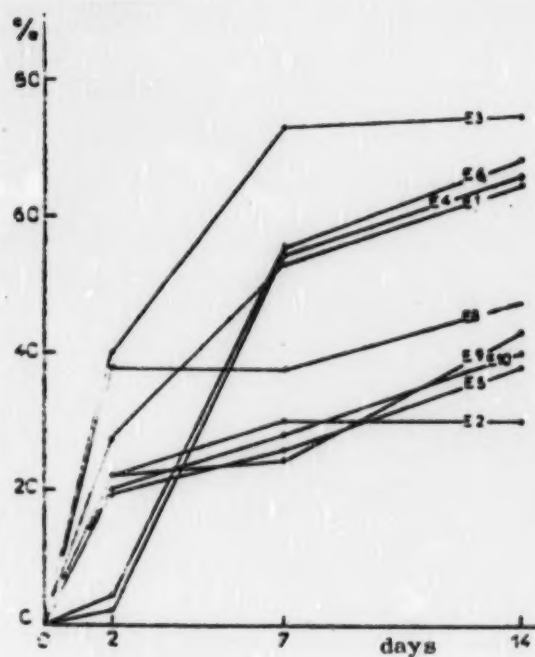
(c) Product elimination rate.

We have not studied product biodegradability. But it is a fact that the emulsifiers contain significant parts of light solvents that are eliminated from the natural environment by simple evaporation. Figures 8, 9, 10, 11, 12, and 13 show this type of elimination. The following facts too are pertinent.

Most of the volatile solvents are eliminated in a few days. In two days 15% of the products lost 40% of their organic matter oxydizable into sulfuric dichromate. Forty-eight percent of the products reach this same threshold in seven days, and 62% do so in two weeks.

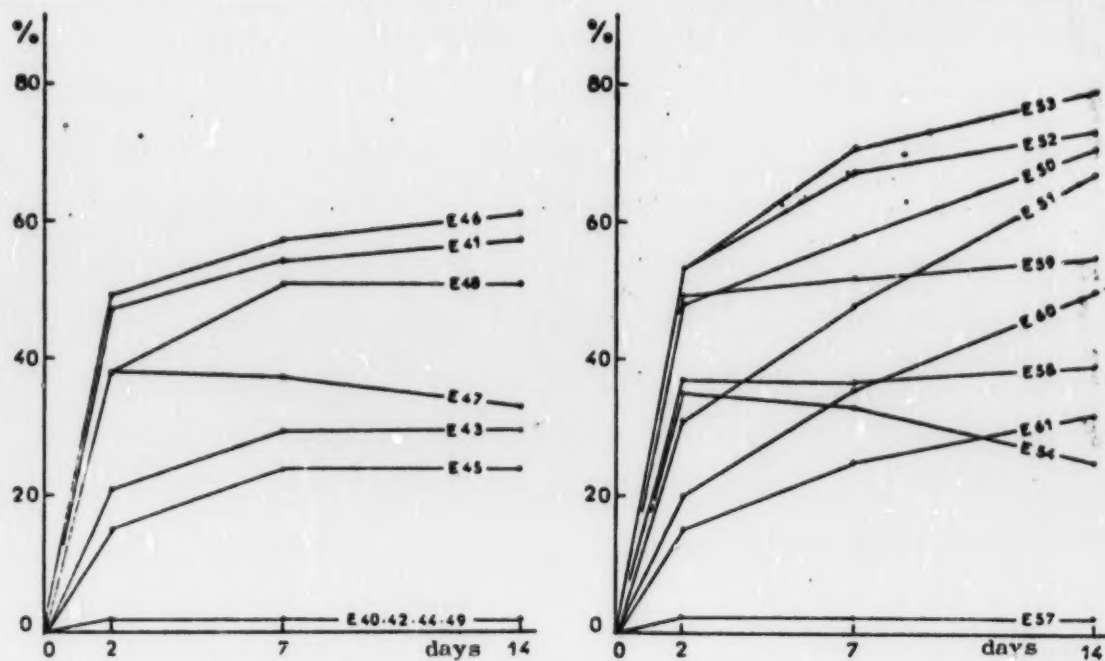
These solvents most often make up between 30% and 80% of the input of degradable organic matter from the emulsifiers. If one accepts the fact that the light solvents rather favor product efficiency, it then is interesting to point out that these are the same products the natural environment rids itself of the most readily. On the other hand, there are certain other emulsifiers with heavy solvent bases, or no solvents at all, that are not so eliminated. Here one must wait for bacterial degradation, and this takes longer. If, for once, efficiency leans toward a lesser nuisance to the environment, something that is rare indeed, then it merits being pointed out.

The curves for each of the products tell us the rate and final amount of environmental purification that takes place. That part eliminated in the first week contains the volatile solvents, that in the second week the heavy solvents, or the detergents themselves. The study of the kinetics of the elimination of the products by the natural environment thus contains interesting information, and it will be desirable to select those products



Figures 8, 9, 10, 11. Kinetics of elimination for products E_1 to E_{10} (left, top), E_{11} to E_{20} (right, top), E_{21} to E_{29} (left, bottom), and E_{30} to E_{39} (right, bottom).

that eliminate themselves the best from among products with like efficiencies and toxicities.



Figures 12 and 13. Kinetics of elimination for products E_{40} to E_{49} (left), and E_{50} to E_{61} (right).

II. Pulverulant products.

Pulverulant products will be used differently, depending on their density, when eliminating hydrocarbons at sea. The heavier ones will take the oil to the bottom, while the others will form agglomerates on the surface for later recovery. These two modes have initial absorption of the oil in common, however. Accordingly, we studied agglomerants and precipitants in the same way.

1. Bibliographic review.

Whereas some of these products have been rather widely used

at sea when it was required to eliminate oil slicks, there have been few laboratory studies, on the other hand, for use in testing their absorption capacity. O. Sturz and K. Klein (1964) used diesel engine oils and fuels as a reference and made a direct volumetric measurement to obtain the difference in the quantity of hydrocarbons retained per 100 grams of powder. They then measured the salting out that occurred as a result of the pressurized circulation of water through the agglomerate. Later on, F. Edeline (1970), studying the scrubbing of water after use in the steel industry, recommends a method that approaches **natural conditions** more closely. He proposes the use of a 1.10 m diameter basin, agitation, and hydrocarbon recovery methods using Soxhlet extraction methods, which are quite lengthy. Finally, G. Neirinckx (1970) filtered an agglomerate formed under different conditions, but with an excess of oil, under vacuum and measured volumetrically the quantity of oil salted out.

2. Choice of methods used.

It is practically impossible to use methods recommended for the much less viscous lubricants and fuels to cope with crude oil. This is why we did not use the O. Sturz and K. Klein method. That of F. Edeline, while highly complicated, is justified solely because it can be used to make precise studies of thin films of residual oil. We thus preferred to use G. Neirinckx's method, which is simple and can, after some adaptation, be used to obtain more exact results. We measured three parameters: hydrophilic capacity; oleophylic capacity; and salting out.

3. Methodology.

(a) Hydrophylic capacity measurement.

A filtering cylinder (L = 115 mm, ID = 31 mm) is used. The No. 3 fritted glass bottom is covered with filter paper disk.

The white value was obtained by passing 10 ml of distilled water at a reduced pressure and, after the walls were wiped, weighing the empty receptacle, which we shall call P_1 . One gram of powder then was placed in the receptacle and covered with water. The mixture then was filtered as before after 30 seconds of contact, and the receptacle was weighed once again. This weight we shall call P_2 . The hydrophylic capacity then can be expressed as a percentage of the water absorbed

$$\text{Hydrophylic capacity} = [P_2 - (1 + P_1)]100 .$$

(b) Oleophylic capacity measurement.

The same measurements as described above are made, except that Saharan oil is used in place of the distilled water. In this case

P_1' is the weight of the frit and filter impregnated with oil;

P_2' is the weight of the whole after passage of the oil.

It is calculated in the form

$$\text{Oleophylic capacity} = [P_2' - (1 + P_1')]100 .$$

(c) Salting out measurement.

The principle involved is that of fixing the oil as above and then washing with 100 ml of sea water. It is impossible to make a gravimetric measure because now the powder is impregnated with oil and water. Colorimetry is used after chloroform extraction of the fixed oil. The weight of oil remaining fixed is calculated by comparison with a standard scale after subtracting the white value. The percentage of oil salted out is readily calculated by comparing with the oleophylic capacity.

4. Results and interpretation.

Table 3 lists the characteristics of the different products when used with Saharan oil, as well as the apparent density measurements.

Product number	Hydrophylic capacity, %	Oleophylic capacity, %	Salting out, %	Apparent density
(a) Agglomerates				
A. 1	17	90	27	0.31
A. 2	20	137	51	0.34
A. 3	62	153	0	0.09
A. 4	80	273	32	0.12
A. 5	224	242	42	0.12
A. 6	90	298	31	0.08
A. 7	24	91	43	0.31
A. 8	107	240	46	0.08
A. 10	138	151	48	0.14
A. 11	176	182	56	0.13
A. 12	160	156	55	0.11
A. 13	131	116	35	0.08
A. 14	376	704	78	0.04
A. 15	332	530	59	0.04
A. 16	131	240	57	0.07
A. 17	28	154	39	0.24
A. 18	30	50	42	0.35
A. 19	0	31	74	0.30
A. 20	30	84	10	0.24
A. 21	83	436	55	0.06
A. 22	39	210	70	0.29
A. 23	32	146	28	0.29
(b) Precipitants				
P. 1	29	30	50	0.80
P. 2	3	52	55	0.73
P. 3	43	62	80	0.57
P. 4	10	18	88	0.97
P. 5	53	47	59	0.57
P. 6	34	53	50	0.84
P. 7	6	38	84	1.32
P. 8	61	135	44	0.21
P. 9	25	53	64	0.83
P. 10	18	36	86	1.01
P. 11	45	52	63	0.54
P. 12	12	33	90	1.06
P. 13	10	28	10	0.92
P. 14	10	104	83	0.83
P. 15	53	63	4	0.56
P. 16	8	23	78	0.53
P. 17	4	26	69	0.52

Table 3.

The apparent density goes a long way toward explaining the properties of these powders. Some thought also should be given to storage, and it would be wise to recognize the fact that one ton of product takes up a good deal of space (in extreme cases as much as 25 m³).

The oleophylic capacity, overall, is greater than 100% for the agglomerates, and can be as high as 500% and 700%. Precipitants have a sharply lower absorption capacity, generally from 30% to 60%. The manufacturers consider treatment designed to make hydrophobic products important. This is a factor that can be important when thin oil films must be eliminated, for it enables products that may have been spread too widely to retain their oleophylic properties until they come in contact with the hydrocarbon that must be eliminated. Our tests, on the other hand, show this advantage to be less evident when treating large quantities of oil, because there is no appreciable increase in absorption capacity, and salting out is not necessarily reduced. There is, on the other hand, a concept that we deem to be more important, and that is the specific surface of the powders. As a matter of fact, the absorption capacities of products of the same type in water and in oil vary greatly according to particle size, porosity, and apparent density. Readily understandable is the fact that powders with a density of a few tens of grams per liter occupy a much greater volume than ordinary powders, weights being equal, and so have no difficulty in absorbing a much greater weight of oil by capillarity. This also explains why precipitants, which necessarily must have a greater density, have an oleophylic capacity that is less than that of the agglomerates by a factor, on the average, of 5.

5. Advantages and inconveniences of pulverulant products.

There is no way to compare such different products, or the so dissimilar results obtained when they are used, as emulsifiers and these products. It is, however, possible to delimit a field of action suitable to the inherent qualities of pulverulant products.

Precipitants are dense powders that take the oil to the bottom. This being the case, all they do is move the pollution around. This is an acceptable procedure when the bottom is very deep, beyond the limits of the continental shelf, for example, but no country is concerned with eliminating oil so far off its own shores. The waters closer inshore are most often exploited for their fish and the accumulation of hydrocarbons in these waters is unacceptable. Some claim that oil thus precipitated is eliminated rapidly. Others claim that the oil, in combination with the precipitant, is an excellent marine fertilizer. Such elimination, and such improvement in the marine soil, remain to be demonstrated, however. The agglomerates, on the other hand, are designed to do away with the hydrocarbons. They are, in principle, preferable, but difficulties are great once they are put to work. First of all, the very lightness that is at the very basis of their special properties makes them very inconvenient to use when winds are high. Moreover, the consistency of the agglomerates that are formed is not very great, and there still are no procedures for recovering them at sea. This gap in fact prohibits their use. Despite all of this, they are interesting because there are no secondary nuisances involved, and their use is recommended in all sheltered areas (ports, estuaries, rivers), where the use of the products, and recovery of the agglomerates, is easily accomplished.

Conclusion

There is no such thing as a miracle product for use regardless of the

site, or of the hydrocarbon that must be eliminated, even if the only consideration is efficiency. The agglomerates in powder form would be the materials of choice if certain problems involved in using them could be resolved. But spreading them on oil slicks is at the whim of the winds, and this reduces their efficiency substantially. Agglomerates can be picked up only when the seas are relatively calm, and the surface covered is small in area. But even when such recovery is possible the residues are bulky, and are practically unrecoverable.

Nor are the precipitants easy to use. These must be finely powdered, and this makes them equally subject to the wind. On the other hand, a significant quantity of the precipitated oil then is salted out progressively and can pollute quite a long stretch of coast because sea currents and winds can change direction during the salting out process.

Given the actual means available to do the work, emulsifiers then become the easiest agents to use. They can be used with equal ease on the high seas or in protected areas, on floating oil, or on the beaches. Only their eventual toxicity can hamper their use when marine flora and fauna must be protected, shellfish areas, for example. Most emulsifiers are efficient when used with certain categories of oil. But according to our tests there are few that are efficient in all cases, particularly where viscous oils are concerned.

The number of usable products is reduced even further when it comes to using products that are efficient yet harmless to marine organisms.

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